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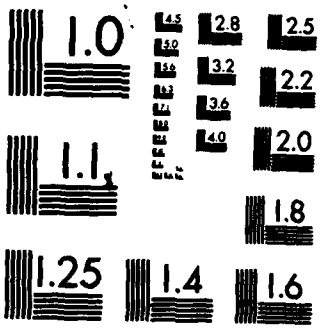


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# Plasma-Enhanced Deposition and Processing of Transition Metal Silicides

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FINAL REPORT

Dennis W. Hess

April 25, 1983

U.S. ARMY RESEARCH OFFICE

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20. Abstract

Radiofrequency (rf) discharges of tungsten hexafluoxide/hydrogen or molybdenum/hexafluoride/hydrogen have been used to deposit films of tungsten or molybdenum. The tungsten depositions resulted in high purity films with as-deposited resistivities ranging from 40 to 170 μΩ-cm, depending upon the deposition conditions. Short (<20 min) heat treatments in hydrogen/nitrogen atmospheres at temperatures above 700°C resulted in a decrease in the resistivity of the films to ~ 8 μΩ-cm, essentially independent of the initial film resistivity. Unlike tungsten, molybdenum films displayed high (>10,000 μΩ-cm) resistivities. These results were due to ~15 atomic percent fluorine incorporated into the film structure during deposition.

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## PROBLEM STATEMENT

As silicon device geometries shrink to less than one micron in size, an increasing burden is placed upon the materials used for gates, interconnects, and contacts in MOS circuits. For the past decade, heavily doped polycrystalline silicon and/or aluminum have been the preferred materials for these applications. However, polysilicon is a relatively high resistivity material, thereby reducing speed, and aluminum is a low melting material, thereby limiting processing latitude. As a result, transition metals and transition metal silicides are being studied as possible replacements for current interconnect technology. The following report describes an initial investigation of the use of rf glow discharges (plasmas) for the deposition of tungsten and molybdenum films. Chemical, physical, and electrical properties of the films are reported as a function of plasma deposition parameters.

# INTRODUCTION

The tremendous increase in complexity of integrated circuits (IC's) over the past decade has in large part been made possible by the continual decrease in circuit element or pattern size. As device geometries shrink still further (to 1 μm and less), increasing demands are placed upon the materials used for interconnections and gates in metal-oxide-semiconductor (MOS) circuits. For instance, these materials must possess low resistivity, tolerate high (>600°C) processing temperatures, and be capable of precise and reproducible pattern definition at the 1 μm level.

Since the late 1960's, the material which has been most widely used for interconnect applications is polycrystalline silicon (1). Several reasons exist for its wide utility in this regard. The process technology required for reproducible and controllable deposition of polysilicon is well-established and reasonably well-understood. Also, polysilicon is capable of withstanding high processing temperatures, and can be patterned with existing etchants. Finally, thermal oxidation of polysilicon is easily performed, and the resulting oxide is an insulator with low conductivity, low pinhole density, and excellent adhesion. Therefore this thermal oxide can be used for masking purposes during polysilicon etching, as well as for dielectric isolation between subsequent films deposited over polysilicon.

However, silicon-gate technology presents several limitations for future (and in some cases present-day) circuits. First, the speed of a circuit is related to the sheet resistance of the interconnect lines. For polysilicon of 0.4 μm thickness and 3-5 μm width, sheet resistance is fairly high (usually ~ 20 Ω/□ ), and so the propagation delay is high also. Secondly, as devices are scaled to smaller lateral dimensions, the

vertical dimensions must also shrink if fine pattern sizes are to be controllably delineated. Thus, sheet resistance increases further, as does the propagation delay. Finally, since the grain size of polysilicon is typically ~ 0.1 μm (2) under current process conditions, very small lines with straight edges are difficult to achieve.

Currently, two approaches are being pursued to eliminate the disadvantages incurred in polysilicon technology. The first of these involves the use of refractory metals such as molybdenum tantalum, and tungsten (3-11). Deposition techniques utilized for such films include electron beam evaporation (5,6) sputtering (3-5), and chemical vapor deposition (7-11). The resulting films have proved useful for MOS devices insofar as they can be patterned reproducibly (small grain sizes), and their sheet resistances are ~ 0.3 Ω/□ , a decrease of ~ 100 compared to polysilicon. However, these metals have higher work functions than does doped polysilicon, and so threshold voltages are naturally higher for unimplanted NMOS circuits. Further, a doped oxide glass must be used for dielectric isolation of the refractory metals from subsequently deposited conducting films, since thermal oxides of these refractory metals are poor dielectric and passivation layers. Finally, these metals are not, in general, resistant to chemical reagents or oxidizing atmospheres used for device processing.

The second approach to interconnection technology involves the use of metal silicides (12-17). These materials have been deposited by electron beam evaporation, sputtering (17), and, most recently, by plasma-enhanced CVD (18). Resistivities of such silicides as $TaSi_2$, $TiSi_2$, $MoSi_2$, and $WSi_2$ are in the range of 25-100 μΩ-cm (17), which is a factor of 5-10 lower than that of heavily doped polysilicon.

In addition to the low resistivities and small grain sizes displayed by certain metal silicides, these materials also offer some advantages over refractory metals. For instance, oxidation of the silicides results in a uniform, adherent film of silicon dioxide (14,19,20). Further, the silicides are relatively inert to normal chemical reagents used for IC processing.

Plasma-enhanced chemical vapor deposition (PECVD) has been shown to be an extremely useful technique for the deposition of inorganic films (e.g., $SiO_2$ and $Si_3N_4$) for IC applications. The results described below indicate the applicability of a glow discharge to transition metal film formation.

## RESEARCH SUMMARY

### Film Deposition

A radial flow parallel plate plasma-enhanced deposition (and etching) system was designed and constructed as shown in Fig. 1. The electrodes are 7-in. diameter, with the upper electrode powered. The lower electrode is grounded and can be heated via a resistance heater. The electrode spacing is 2-in, but can be varied. Pressure is measured with a capacitance manometer. Total flow rates of 40 sccm are set with mass flowmeters. The pumping system consists of a 50 cfm corrosion resistant pump with a liquid nitrogen trap placed between the pump and the vacuum chamber. A throttling valve allows independent control of the pressure and the flow rate. Unless otherwise indicated, the following conditions were used for the depositions discussed below: frequency = 4.5 MHz; electrode temperature = 350°C; pressure = 200 mtorr; power = 0.06 W/cm$^2$; $H_2/WF_6$ = 3.

Pure $WF_6$ was found unsuitable as a source gas, since etching was favored over deposition above 90°C. Films could be formed at temperatures

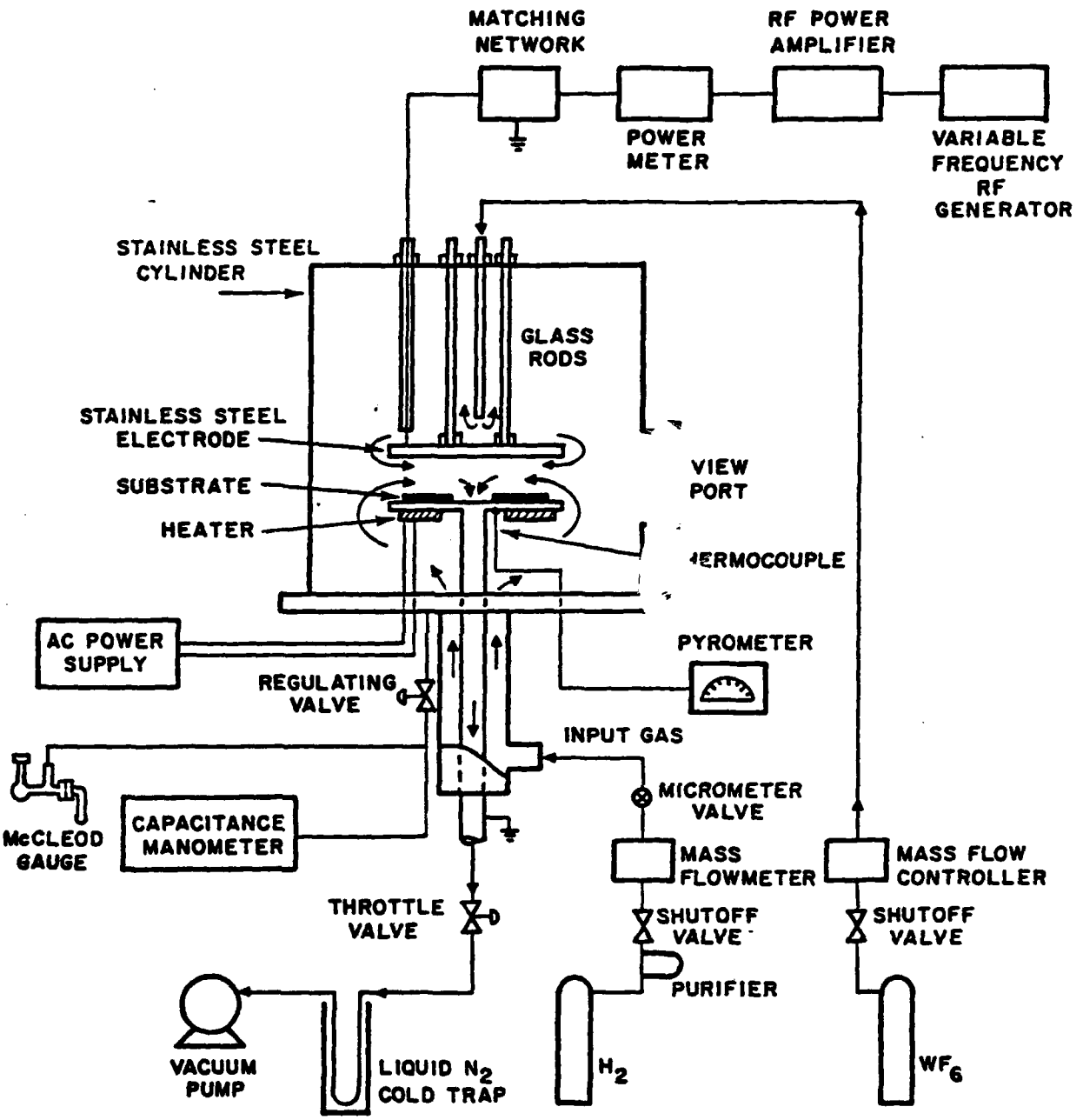


Fig. 1. Schematic of plasma-enhanced CVD system

~ 40°C; however, the films were porous, and they possessed large tensile stresses as evidenced by beam bending studies, and by the fact that the films cracked either upon deposition, or after heat treatments at 250°C. Hydrogen additions to $WF_6$ suppresses film etching by reaction with

$$WF_6(g) + 3H_2(g) \rightleftharpoons W(s) + 6\ HF\ (g)$$

fluorine atoms. These additions permit the use of elevated temperatures, and result in smooth, pinhole-free, metallic films of tungsten. An $H_2/WF_6$ ratio of 3/1 was therefore generally used for stoichiometric reasons. Higher ratios resulted in lowered deposition rates due to dilution effects. For instance, under our standard deposition conditions, and $H_2/WF_6$ ratios of 1.5/1, 3/1, and 6/1, the deposition rates are 6.5, 4.0, and 2.2 nm/min, respectively.

It should be noted that the high concentration of fluorine atoms generated in $WF_6$ or even $WF_6/H_2$ plasmas can result in significant etching of Si or even $SiO_2$ exposed to these discharges. Since deposition temperatures are in excess of 300°C, more than 50 nm of $SiO_2$ can be etched away during the initial deposition period in $WF_6/H_2$ discharges.

As-deposited sheet resistivities determined by four-point probe measurements of tungsten films deposited at 300°C are shown in Fig. 2, along with similar results reported by other researchers. In general, the high-temperature deposits (hot and cold wall CVD at 400 - 800°C) show the lowest resistivity, while the lower temperature depositions (e-beam evaporated (200°C) and the present PECVD) show the highest resistivity. Such results are probably due to larger grain size and lower defect and impurity incorporation in the higher temperature deposits. These observations suggest that the PECVD films have high purity, and indeed, Auger studies confirm this speculation (21).

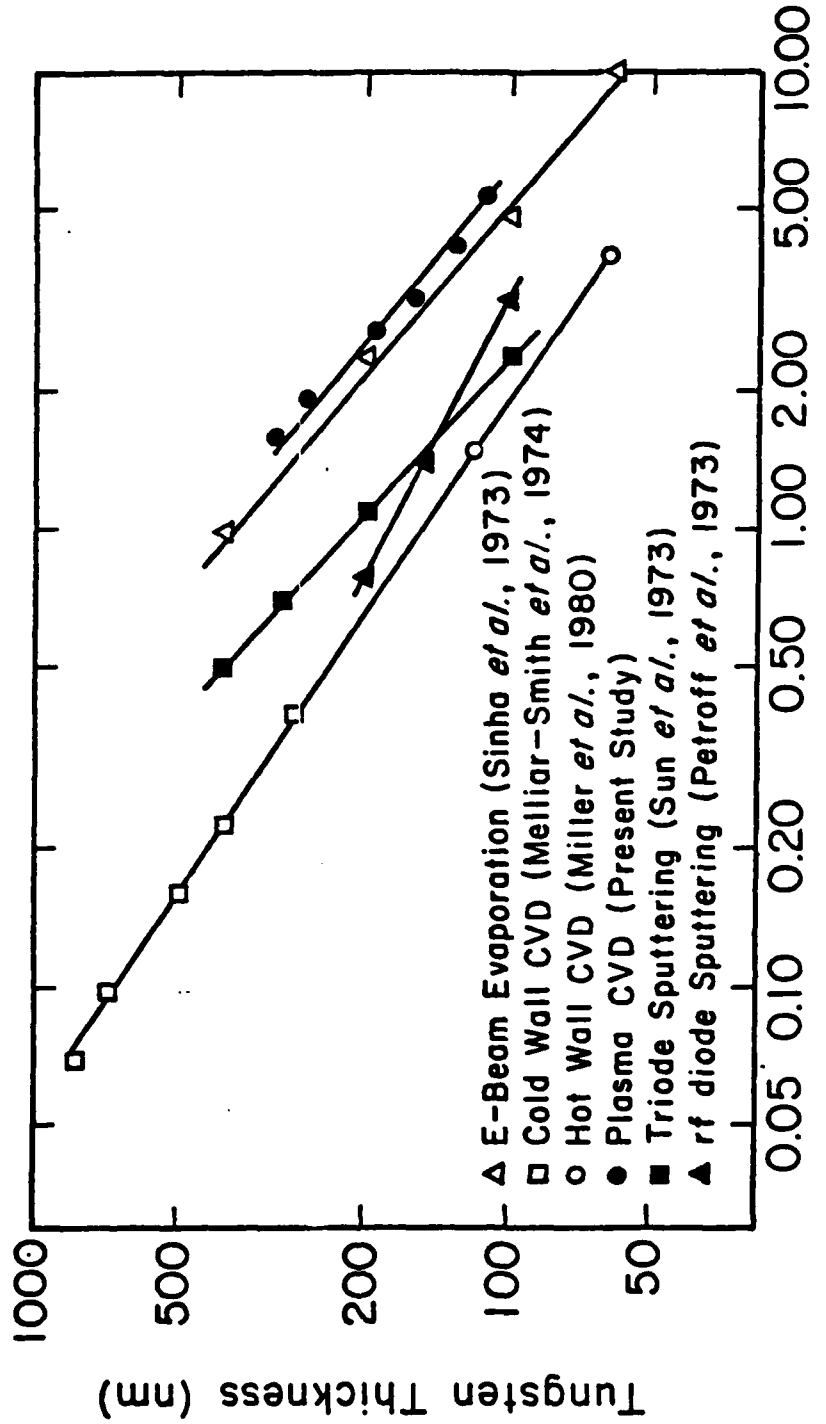


Fig. 2. Comparison of sheet resistivity versus film thickness for PECVD and other deposition techniques for tungsten films.

Although small amounts of $SiF_4$ noted in the source gases did not present an appreciable problem, other impurities did. Deposition rates were found to be most consistent within any one lecture bottle of $WF_6$. However, variations up to a factor of two in deposition rate were observed with different bottles (independent of gas supplier). High resolution mass spectrometry was unable to detect impurities that might be responsible for such differences. Further, no changes were observed in as-deposited (or annealed) resistivities, even when deposition rates varied by a factor of two. Apparently, trace impurities (perhaps $O_2$ or $H_2O$ which were masked by the mass spectrometer background) were present which affected adsorption of $WF_x$ fragments, but were not incorporated in the film. Such conclusions are consistent with previous studies that indicate a surface poisoning and hence a lowered deposition rate when HCl, $O_2$, and $H_2O$ were present during tungsten CVD (22).

In addition to $SiF_4$, small concentrations of methylated fluorosilanes ($SiCH_3F_3$ and $Si(CH_3)_2F_2$) were generally present in $WF_6$ source gases. These carbon-containing compounds may be responsible for the slightly higher observed resistivity (compared to other low temperature techniques such as sputtering and e-beam evaporation; see Fig. 2, for example). Further evidence for such speculations arise from results obtained with one lecture bottle of $WF_6$. This particular cylinder generated 0.2 μm films with sheet resistivities >10 Ω/□ . High resolution mass spectra of this source material showed factors of 5 increases in $Si(CH_3)F_3$ and $Si(CH_3)F_2$ over the more normal source bottles.

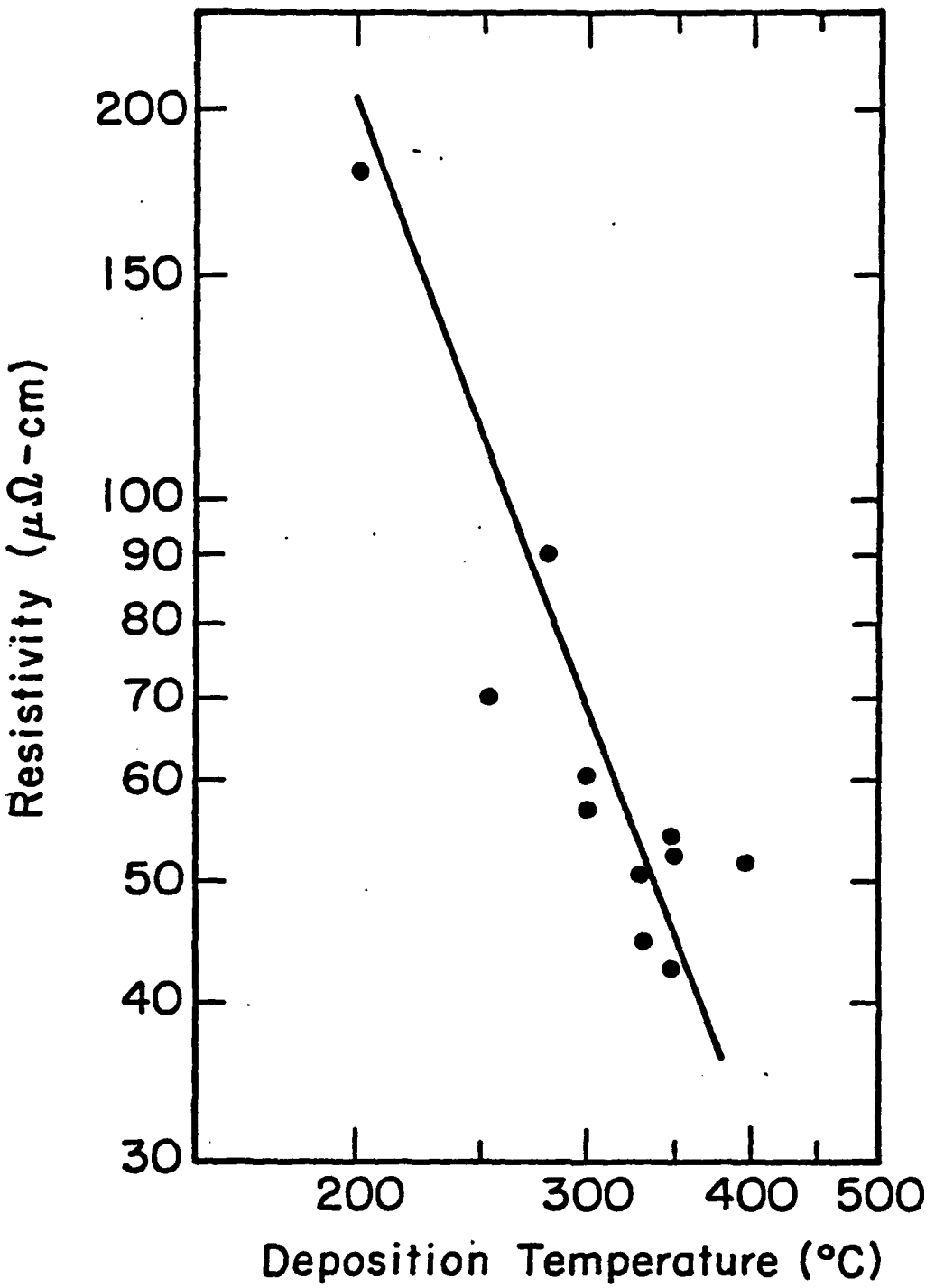


Fig. 3 . Dependence of W film resistivity on electrode temperature. Film thicknesses ranged from 200 nm to 340 nm.

## Film Characteristics

### Resistivity

As shown in Fig, 2, the sheet resistivities of PECVD tungsten films decreased with increasing film thickness. Resistivities were also observed to decrease with increasing electrode temperature (Fig. 3). These results are consistent with similar studies on triode-sputtered (23) and e-beam evaporated films (24).

The adhesion of PECVD tungsten films to thermal $SiO_2$ was generally poor. Elevated (>600°C) temperature heat treatments typically resulted in films peeling from the $SiO_2$. Such effects are apparently due to the fact that tungsten cannot reduce $SiO_2$ to form a strong bond to silicon, and to the wide difference in thermal expansion coefficient between $SiO_2$ and W. Adhesion was found to be quite good on borosilicate glass. Unfortunately, these substrates could not withstand high (>900°C) temperatures. Sapphire was ultimately chosen as the substrate for annealing studies, since its thermal expansion coefficient closely matches that of tungsten. No cracking or peeling was observed on any tungsten film deposited on sapphire and annealed in the temperature range of 650° - 1100°C.

Elevated temperature heat treatments in forming gas (10% $H_2$/90%/$N_2$) resulted in a lowering of the resistivity of PECVD films. Figure 4 indicates that temperatures above 650°C result in a very rapid decrease in resistivity. Preliminary scanning electron microscope photographs suggest that such effects are not primarily due to grain growth. At an electrode temperature of 350°C, the grain size is estimated to be ~ 300Å, while after a 900°C heat treatment in forming gas for 30 min., the grain size was ~ 700Å. Rather, the rapid decrease in resistivity upon high

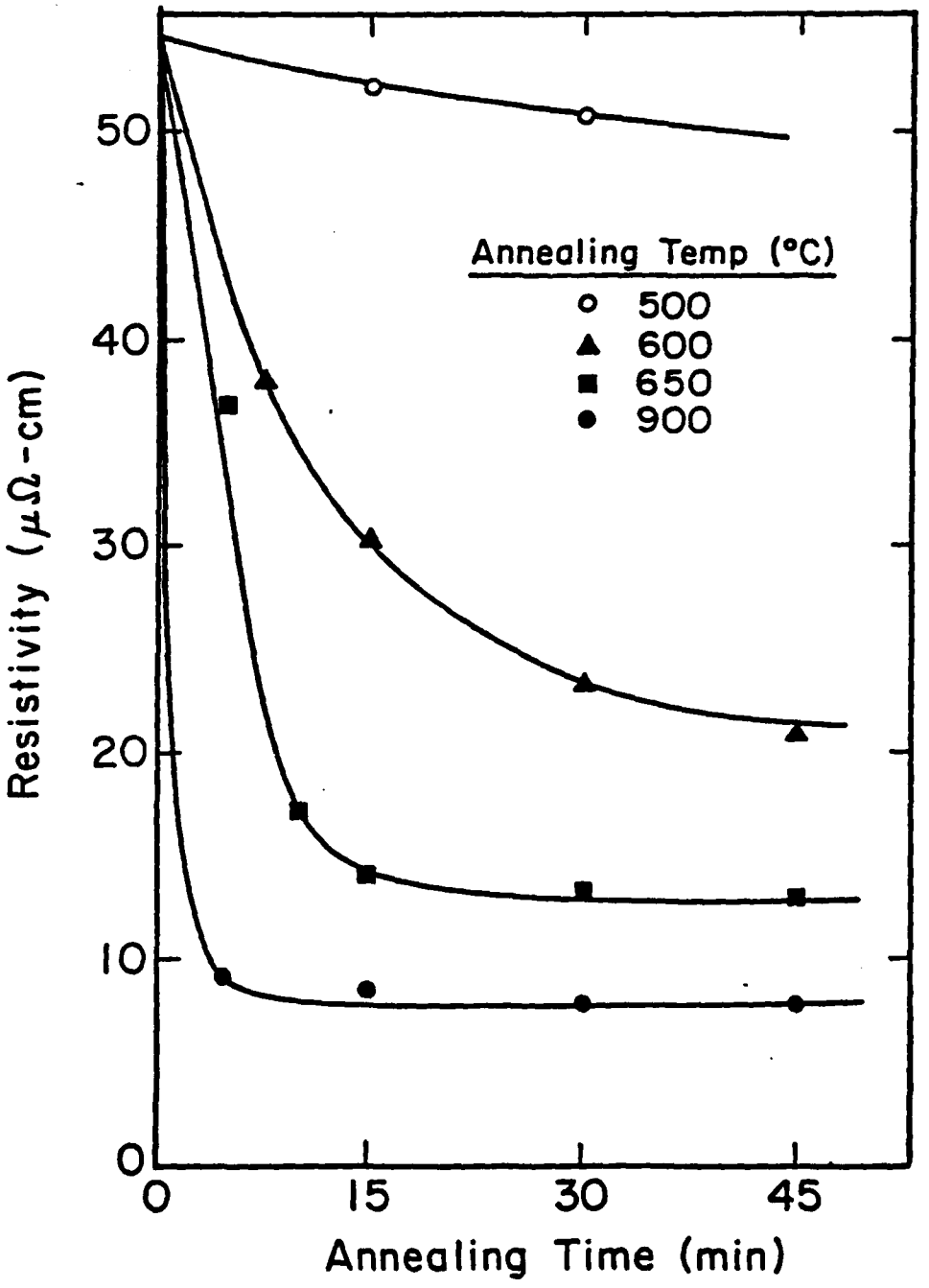


Fig. 4. Dependence of W film resistivity on annealing time and temperature.

temperature heat treatment may be due to outdiffusion of fluorine or to annealing of radiation-induced defects (incurred during deposition).

Initial resistivity of the PECVD tungsten films also depended upon the $H_2/WF_6$ ratio as shown in Fig. 5. Nevertheless, short heat treatments rapidly decreased the resistivity. In fact, if the source gases were pure, short (<15 min.) heat treatments above 900°C always resulted in resistivities ~ 8 μΩ-cm).

A narrow range of rf frequencies were studied. Between 4.5 and 20 MHz, the as-deposited resistivity increased by ~ 30% as the frequency increased. This trend is consistent with enhanced ion bombardment at the lower frequencies, which could assist the desorption of fluorine from the growing tungsten film, although chemical effects involving the generation of different concentrations of $WF_x$ fragments cannot be discounted. Again, when post-deposition heat treatments above 800°C were invoked, resistivities dropped to 8 μΩ-cm.

Stress

Stress measurements were performed on the tungsten films by depositing them onto thin borosilicate glass beams (12 x 60 x 0.15 mm), and measuring the radius of curvature of the beams by use of a metallurgical microscope. The stress decreased from ~ $9.5 \times 10^9$ dynes/cm$^2$ (tensile) at a frequency of 20 MHz to ~ $1.5 \times 10^9$ dynes/cm$^2$ (tensile) at 4.5 MHz. Such trends are consistent with those observed on PECVD silicon nitride (25), and are probably due to enhanced ion bombardment at low frequencies. At the lower frequencies, no cracking of the films was observed, even when heat treated at 1100°C for 30 min.

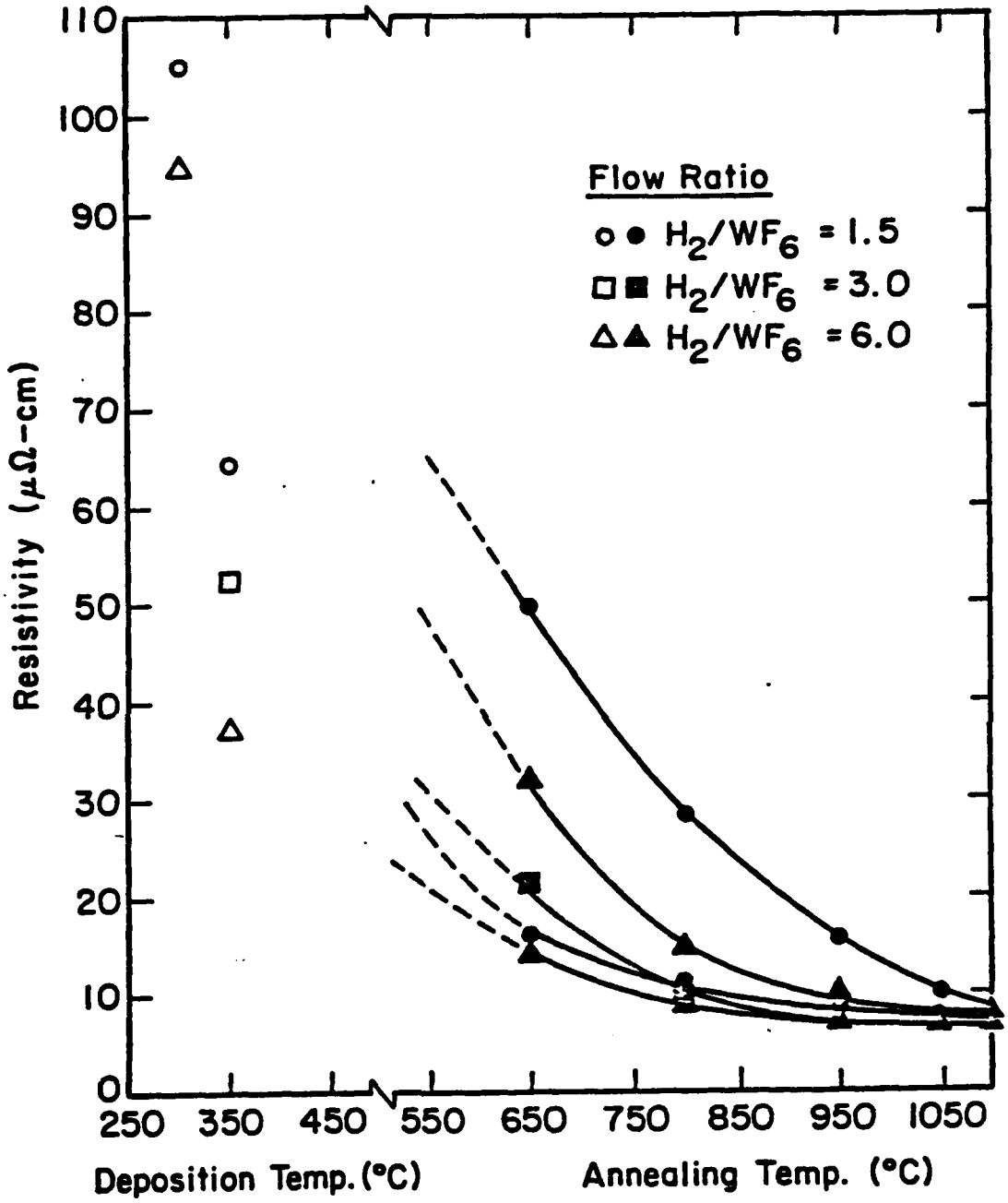


Fig. 5. Dependence of W film resistivity on $H_2/WF_6$ deposition ratio and on annealing temperature. The annealing atmosphere was forming gas.

### Work Function

Using MOS capacitors with varying $SiO_2$ thicknesses, the work function of PECVD tungsten films was determined (26,27). For our standard deposition conditions, the work function was found to be 4.4 eV, which is in good agreement with a reported value of 4.5 eV for bulk tungsten (28).

### Step Coverage

Preliminary studies of the ability of PECVD tungsten films to cover silicon steps are most encouraging. A 300 nm tungsten film, deposited under our standard set of conditions, displayed conformal coverage of an 1800 nm silicon step (~ 80° angle) etched into single crystal silicon. In large part, these results are probably a result of surface-reaction rate control in the PECVD process.

### Etching Characteristics

Introductory etching investigations were performed on PECVD tungsten films using $CF_4/O_2$ and $SF_6/O_2$ plasmas. The films etched at ~ 40 nm/min in $CF_4$/10% $O_2$ and ~ 70 nm/min in $SF_6$/10% $O_2$. Optical emission studies suggest that fluorine atoms are the primary etchant for tungsten films.

## Molybdenum Depositions

Preliminary depositions were carried out using $MoF_6$ and $H_2$ at temperatures above 200°C. When the $H_2/MoF_6$ ratio was less than 4/1, the deposited films oxidized readily during exposure to ambient conditions. At a $H_2/MoF_6$ ratio of 7/1, molybdenum films that resisted oxidation could be formed. However, the as-deposited resistivities were high (>10,000 μΩ-cm). Auger analyses demonstrated that this resistivity was the result of fluorine incorporation into the film during deposition; typical fluorine

concentrations were ~ 15 atomic percent. Initially, This result is surprising, since the W-F bond is stronger than the Mo-F bond (29,30). However, $MoF_3$ is a stable, non-volatile compound below 800°C. As a result, as the electron impact dissociation of $MoF_6$ proceeds at temperatures below 400°C, any $MoF_3$ formed is incorporated into the growing film. Large concentrations of fluorine are thus found in PECVD films, resulting in high resistivities.

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